Macroscopic Quantum Oscillations of Antiferromagnetic Nanoclusters in a Swept Magnetic Field

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New macroscopic quantum interference effects in the behavior of the antiferromagnetic nanoclusters under action of a swept magnetic field are predicted and theoretically investigated, namely : oscillations of the magnetic susceptibility of nanocluster similar to the electron Bloch oscillations in crystal and the corresponding Stark ladder-like resonances in ac-magnetic field. These effects are related to that of the macroscopic quantum coherence phenomena. The analogy of the antiferromagnetic nanoclusters quantum behavior and Josephson junction with a small capacity was revealed as well.

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The quantum dynamics of magnetic nanoclusters with a large spin is drawing increasing attention, both from experiment and theory. Fundamental scientific questions at stake are the macroscopic quantum phenomena including the macroscopic tunneling and interference of wave functions and the transition from quantum to classical behavior – a process known as decoherence. From this point of view metallorganic molecules with large number of d-ions (Fe, Mn, Co etc) such as Mn_{12}, Fe_8, Fe_{10} are of particular interest. The presence of strong enough antiferromagnetic interaction between d-ions is a characteristic feature of these objects. Some of these clusters have the magnetic structure of the ferrimagnetic type (Mn_{12}, Fe_8) with large spin moment in the ground state ($S = 10$). As of now the quantum mechanical properties of these nanoclusters are investigated in great detail. Recently such new phenomena and specific features as molecular bistability [1], macroscopic quantum tunneling of magnetization, quantum hysteresis [2–4], the appearance of Berri–phase [5] and quantum peculiarity of magnetic susceptibility behavior [6], have been discovered and predicted. The quantum properties of nanoclusters with magnetic structure of antiferromagnet type (Fe_{10}, Fe_6) are less well understood [7]. The aim of the present paper is the investigation of macroscopic quantum dynamics phenomena of the antiferromagnetic clusters in a swept magnetic field. The reason to use the swept field is that it produces a torque on the spin system of the antiferromagnetic molecules accelerating the spin precession and displays a new macroscopic quantum interference effects in their behavior.

We consider the ring-like molecular magnets (Fe_{10}, Fe_6, Fe_{18}) composed of $N = 2k$ d–ions spaced on a circle lying in the xy-plane; there is an antiferromagnetic exchange interaction between them. The Hamiltonian of this system can be represented as

$$\mathcal{H} = J \left(\sum_{i=1}^{N-1} \vec{S}_i \vec{S}_{i+1} + \vec{S}_1 \vec{S}_N \right) + \sum_{i=1}^{N} H_{cr}(S_i) + g\mu_B \sum_{i=1}^{N} \vec{S}_i \vec{B}, \tag{1}$$

where $J > 0$ is the exchange interaction constant, $H_{cr}(S_i)$ is the crystal field acting on i-th spin ($H_{cr} = K_1 S_z^2 + K_2(S_x^2 - S_y^2)$, with z-axis directed perpendicular to a molecule plane); for Fe^{3+} $S = 5/2$. In accordance with experimental results it will be assumed that $J \gg K$ (the typical values are $J \sim 10$ cm^{-1}, $K \leq 1$ cm^{-1}). The anisotropy in the plane(K_2) can be formed artificially, e.g. by means of external electric or magnetic fields, pressure, or using anisotropic substrate. Due to C_n-symmetry there is also "n-gonal anisotropy in the plane"($n = 6(10)$ for $Fe_{6(10)}$). Following analysis can be easily reformulated to take into account this anisotropy. Let suppose that the magnetic field is $\vec{B} = (0, 0, B_z)$, where B_z depends on time generally. We decompose as usually for antiferromagnets the local spins into the two subsystems ("sublattices") and it is reasonable to assume the coordinates of two magnetic sublattices, describing the macroscopic quantum behavior of the antiferromagnetic molecule as degrees of freedom. In order to describe such system the coherent quantum states will be used [8]

$$|\theta_1, \varphi_1; \theta_2, \varphi_2\rangle, \tag{2}$$

where θ_i, φ_i are the polar and azimuthal angles of the spin of the magnetic sublattices. (These angles are measured from the z and x axes respectively). The Lagrangian of the system can be represented as:

$$L = -\frac{M}{\gamma} \sum_{i=1}^{2} \cos\theta_i \dot{\varphi}_i + B_z M \sum_{i=1}^{2} \cos\theta_i - \frac{1}{2} K_u \sum_{i=1}^{2} \sin^2\theta_i - \frac{1}{2} K_\perp \sum_{i=1}^{2} \sin^2\theta_i \sin^2\varphi_i - NJS^2 \Big[\cos(\theta_1 + \theta_2)$$

$$+ \sin\theta_1 \sin\theta_2 \big(1 + \cos(\varphi_1 - \varphi_2) \big) \Big], \tag{3}$$

where $M = 1/2g\mu_B SN$, $\gamma = g\mu B/\hbar$, $K_u = NK_1 S^2$, $K_\perp = 1/2NK_2 S^2$.

This Lagrangian can be derived by means of the standard technique of coherent quantum states (see for example [9]). All terms in (3) are of apparent physical meaning. The first term is called Wess-Zumino term (kinetic energy), the second term is Zeeman energy, the third and fourth term are the magnetic anisotropy and the fifth is the exchange interaction energy.

Furthermore it is convenient to use the new variables:

$$\theta = \frac{\theta_1 + \theta_2}{2}, \quad \varphi = \frac{\varphi_1 + \varphi_2 - \pi}{2}, \tag{4}$$

$$\epsilon_1 = \frac{\theta_1 - \theta_2}{2}, \quad \epsilon_2 = \frac{\varphi_1 - \varphi_2 + \pi}{2}, \tag{5}$$

Then the partition function of the system can be represented as the functional integral in the Eucledian space ($\tau = it$).

$$Z = \int D\epsilon_1 D\epsilon_2 \int D\theta D\varphi \, e^{-\int_0^{\hbar\beta} d\tau L(\theta, \varphi, \epsilon_1, \epsilon_2)}. \tag{6}$$

Upon integrating (6) over ϵ_1 and ϵ_2 one can obtain the following effective Lagrangian depending on the variable $\varphi(\tau)$ only:

$$L = \frac{\chi_\perp}{2} \left(\frac{\dot{\varphi}}{\gamma} - B_z \right)^2 + K_\perp \cos^2 \varphi. \tag{7}$$

The total magnetic moment of the antiferromagnetic molecule equals to:

$$M_z = \begin{cases} \chi_\perp \left(B_z - \frac{\dot{\varphi}}{\gamma} \right), & B_z \leq B_c, \\ 2M, & B_z \geq B_c, \end{cases} \tag{8}$$

where

$$\chi_\perp = \frac{Ng^2\mu_B^2}{4J}, \quad B_c = \frac{4JS}{g\mu_B}. \tag{9}$$

The following classical motion equation for variable φ can be put in correspondence to the Lagrangian (7) [9,10]:

$$\frac{\chi_\perp}{\gamma^2} \ddot{\varphi} + \frac{\alpha M}{\gamma} \dot{\varphi} + K_\perp \sin 2\varphi - \frac{\chi_\perp \dot{B}_z}{2\gamma} = 0. \tag{10}$$

Inserted here is the dissipative term $\alpha M\dot{\varphi}/\gamma$ related to the attenuation occurence in Landau–Lifshits equations, where α is the dimensionless Hilbert constant.

For description of the thermodynamical and nonequilibrium properties of the molecule at finite temperature one can utilize the partition function as follows (see for example [12])

$$Z = \int d\varphi_0 \int_{\varphi(0)}^{\varphi(\hbar\beta)} D\varphi(t) \, e^{\frac{S_{eff}[\varphi(\tau)]}{\hbar}}, \tag{11}$$

where the effective action S_{eff} equals to

$$S_{eff}[\varphi(\tau)] = \int_0^{\hbar\beta} d\tau \, L(\varphi, \dot{\varphi}, \tau) + \frac{1}{2} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\tau' \, \alpha(\tau - \tau\prime) \left[\varphi(\tau) - \varphi(\tau') \right]^2, \tag{12}$$

$$\alpha(\tau) = \frac{\alpha M}{2\pi\gamma} \frac{\left(\frac{\pi}{\hbar\beta} \right)^2}{\sin^2 \left(\frac{\pi\tau}{\hbar\beta} \right)}. \tag{13}$$

Henceforward we shall restrict our consideration to the only quantum properties (at $T = 0$ K). The Hamiltonian of the system for the collective variable φ can be obtained from the Lagrangian (7) by the following procedure. The momentum p corresponding to the independent coordinate φ equals to

$$p = \frac{\partial L}{\partial \dot{\varphi}} = \frac{\chi_\perp}{\gamma} \left(\frac{\dot{\varphi}}{\gamma} - B_z \right). \tag{14}$$

By further substituting this expression to the Hamilton function $\mathcal{H} = p\dot{\varphi} - L$ one can obtain

$$\mathcal{H} = \frac{1}{2\chi_\perp} \left(\gamma p + \chi_\perp B_z \right)^2 - \frac{\chi_\perp B_z^2}{2} + U(\varphi). \tag{15}$$

By performing a standard quantization technique which consists in definition of the operators $\hat{p}$ and $\hat{\varphi}$ by means of the commutation rule $[\hat{p}, \hat{\varphi}] = -i\hbar$ we obtain $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial \varphi}$. The magnetic momentum operator is determined as $\hat{M}_z = -\gamma\hat{p}$. Substituting this expression into the Hamilton function (15) yields

$$\mathcal{H} = \frac{1}{2\chi_\perp} \left(M_z - \chi_\perp B_z \right)^2 - \frac{\chi_\perp B_z^2}{2} + U(\varphi). \tag{16}$$

The magnetic moment of the antiferromagnetic molecule and the angular variable φ are the conjugate variables: $\left[\hat{M}_z, \hat{\varphi} \right] = ig\mu_B$.

Let's consider first the case $B_z = 0$. It is important that the equation (16) is isomorphous to the equation of particle in periodic potential, therefore one can use the results known for this model. The eigenstates of the Hamiltonian (16) are the Bloch functions

$$\Psi_{sn}(\varphi + \pi) = e^{i\pi m} \Psi_{sm}(\varphi), \tag{17}$$

where m is an arbitrary real number. By analogy with the term -"charge states" - for similar states in the theory of Josephson effect [12,13] it is possible to call the states (17) as the "continuous spin states". The Schroedinger equation for the Hamiltonian (16) is reduced to the Mathieu equation from the theory of which it follows that the energy spectrum of the Hamiltonian (16) has a band structure, i.e. the eigenvalues of (15) $E_s(m)$ are the functions defined in the appropriate Brillouin zones. At $U(\varphi) \approx 0$ the band structure corresponds to the approximation of free electrons. In this case the energy spectrum is determined approximately by parabolic function

$$E_n(m) \approx \frac{m^2 \left(g\mu_B^2 \right)}{2\chi_\perp} \tag{18}$$

with the forbidden bands on the boundaries of the Brillouin zones: $m_B = s$ $(s = 1, 2, \ldots S_{max})$, where S_{max} is the maximal spin of the molecule. Near the Brillouin zone boundary the wave function can be represented as follows

$$\Psi(\varphi) = u(\varphi) e^{-iEt}, \tag{19}$$

where $u(\varphi) = A_1 e^{im\varphi} + A_2 e^{i(m+2)\varphi}$. The Schroedinger equation for the Hamiltonian (15) can be written as

$$u'' + \left(\mu^2 - 2b^2 \cos 2\tilde{\varphi} \right) u = 0, \tag{20}$$

where

$$\mu^2 = \frac{2\chi_\perp E}{\left(g\mu_B \right)^2}, \, b^2 = \frac{\chi_\perp K_\perp}{2 \left(g\mu_B \right)^2}. \tag{21}$$

Used here is a new variable $\tilde{\varphi} = \varphi + \pi/2$. The sign "$\sim$" will be further omitted. Substituting (19) to (16) yields

$$\mu^2 = \left(\frac{m^2 + (m+2)^2}{2} \pm \sqrt{\frac{\left(m^2 - (m+2)^2 \right)^2}{4} + b^4} \right). \tag{22}$$

In particular from the expression (22) it is clear that at $m_B = 1$ the forbidden band width equals

$$\Delta E_g = \frac{\left(g\mu_B \right)^2}{\chi_\perp} b^2. \tag{23}$$

Equations (18),(20),(22) determine with sufficient accuracy the energy spectrum in the limit of first two Brillouin zones. The forbidden band between $s - 1$ and s bands equals

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$$\Delta E_s \approx \frac{g^2 \mu_B^2}{2\chi_\perp} \left(2b^2\right)^s s^{1-s}. \tag{24}$$

If $B_z \neq 0$ in (16) it is possible to consider $\chi_\perp B_z$ as a classical gauge field. The wave functions of the Hamiltonian (16) can be obtained from equation (17) by means of apparent gauge transformation. The gauge transformation can be presented as follows:

$$\Psi_1(\varphi) \longrightarrow \Psi(\varphi) e^{\theta(\varphi,t)}, \tag{25}$$

Then

$$i\hbar\dot{\Psi}_1 = \left[\frac{1}{2\chi_\perp} \left(\hat{M}_z - g\mu_B \frac{\partial\theta}{\partial\varphi} - \chi_\perp B_z \right)^2 - u(\varphi) - \frac{\chi_\perp B_z^2}{2} + \hbar\dot{\theta} \right] \Psi_1. \tag{26}$$

Assuming $\theta(\varphi, t) = -\frac{\chi_\perp B_z \varphi}{g\mu_B}$, we have (the label "1" of the function Ψ will be further omitted)

$$i\hbar\dot{\Psi} = \left[\frac{M_z^2}{2\chi_\perp} - \frac{K_\perp}{2}\cos 2\varphi - \frac{\hbar\chi_\perp \dot{B}\varphi}{g\mu_B} - \frac{\chi_\perp B_z^2}{2} \right] \Psi. \tag{27}$$

The last term $\frac{\hbar\chi_\perp \dot{B}\varphi}{g\mu_B}$ in equation (27) is playing the same role as energy $-eF \cdot x$ (F characterizes the electrical field and x is the electron coordinate) in the well-known problem of the dynamics of Bloch electron in electrical field.

Let consider the behavior of the molecule magnetization process under the action of time-dependent magnetic field $B_z(t)$ varying adiabatically slowly i.e.

$$\left| \frac{\chi_\perp \dot{B}_z}{g\mu_B} \right| \ll \frac{K_\perp}{\hbar}. \tag{28}$$

To describe the dynamics of the antiferromagnetic vector of the molecule (or "staggered magnetization") let's consider a wave packet of the Bloch functions (19). Let $\bar{m}$ and $\bar{\varphi}$ be mean values of the generalized coordinate and momentum of the packet and the values Δm and $\Delta\varphi$ ($\Delta m \cdot \Delta\varphi \sim 1$) determine the packet width. Under influence of $\dot{B}_z$ which induces the rotational torque accelerating spin precession the wave packet moves to the boundary of Brillouin zone where Bragg reflection takes place. Here the wave packet group velocity changes its sign to an opposite after that a new process of the wave packet acceleration starts.

In mathematical terms this process can be described by the following equations:

$$\dot{\bar{m}} = -\frac{\chi_\perp}{g\mu_B}\dot{B}, \tag{29}$$

$$\dot{\bar{\varphi}} = \frac{1}{\hbar}\frac{\partial E_s(\bar{m})}{\partial\bar{m}}, \tag{30}$$

where $E_s = E_s(\bar{m})$ is energy spectrum of (16) for the s-band. Equations (29,30) must be completed by appropriate initial conditions.

In the adiabatic case the antiferromagnetic molecule remains in the state with the definite s and all observed values as, for example, the magnetization (8), accounting (29,30) are the oscillating functions of time with the frequency

$$f_{Bloch} = \frac{\chi_\perp \dot{B}_z}{g\mu_B} = \frac{g\mu_B \dot{B}_z N}{4J}. \tag{31}$$

These oscillations are identical to the oscillations that electrons are subjected in crystal or superlattice under electrical field [14] (Bloch oscillations). This macroscopic quantum effect is essentially the macroscopic quantum coherence effect induced by time-increasing (decreasing) magnetic field.

If the external field can be represented by the following sum

$$B = B_0 + at + b\sin 2\pi f t, \tag{32}$$

then it is possible to expect the resonance origin at

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$$f = f_{Bloch} \tag{33}$$

and on the frequences $f = r \cdot f_{Bloch}$ as well, where r is a rational number (Stark ladder-like resonances). The constant shifting field B_0 plays here role of a chemical potential and can be used to provide optimal conditions for observing the considered macroscopic quantum effects.

Let's present some numerical estimations. For Fe_6 and Fe_{10} $J =20.9$ cm^{-1} and $J = 9.6$ cm^{-1}, accordingly [15–17]. The magnetic anisotropy is of the "easy plane" type. The constants of anisotropy are $K = -0.3$ cm^{-1}/ion (Fe_6) and $K = -0.1$ cm^{-1}/ion (Fe_{10}). The estimation under the formulas (28-31) gives for Fe_{10}: $B_c = 97$ T; $\omega_E = 1.7 \cdot 10^{13}$ rad/s, $f_{Bl} \approx 10^5$ Hz at $\dot{B}_z = 10^6$ T/s.

Let's examine briefly a role of dissipation. From equation (10) it follows, that the relaxation time of φ angular perturbations equals to $\tau = (\alpha \omega_E)^{-1}$. For observation of the Bloch oscillations it is necessary that $f_{Bloch} > \tau^{-1}$ that restricts the value $\dot{B}_z$ from below. For the relaxation time estimation we shall take an advantage of the experimental data of paper [18] for the antiferromagnet MnF_2 in which the exchange interaction constant, field B_c and consequently ω_E are close to that for the antiferromagnetic molecules in the question. In the [18] the linewidth of antiferromagnetic resonance ΔH was measured which is linked to a Hilbert constant α and relaxation time by the relation $\gamma \Delta H = \alpha \omega_E = 1/\tau$, i.e. $\tau = (\gamma \Delta H)^{-1}$. In agreement to [18] the temperature dependence $\Delta H(T)$ at 5 K–40 K is an average between T^3 and T^4 with the tendency to T^4 (and even T^5) when approaching to $T = 5$ K. At $T = 5$ K $\Delta H \sim 0.1$ Oe, therefore $\tau \approx 0.5 \cdot 10^{-6}$ s. It is possible to expect $\tau > 10^{-3}$ s at 0.5 K.

On the other hand the condition (28) restricts from above the value $\dot{B}_z$. Thus, the following inequality should be fulfilled:

$$\frac{4J}{Ng\mu_B\tau} \ll \dot{B}_z \ll \frac{\gamma K_\perp}{\chi_\perp}. \tag{34}$$

Accepting $K_2 \sim 10^{-4}J$ we shall obtain following boundary values for an area of acceptable $\dot{B}_z$ values: 10^4 T/s and 10^{10} T/s.

In conclusion, it was shown that the external time dependent magnetic field induces new macroscopic quantum effects in the behavior of the antiferromagnetic nanoclusters: oscillations of the magnetization similar to the electron Bloch oscillations in crystal and the corresponding resonances in ac-magnetic field. These effects are related to that of the macroscopic quantum coherence. The analogy of antiferromagnetic nanoclusters quantum behavior and Josephson junction was revealed as well.

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